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Metallacarborane Complexes That Incorporate the Lanthanides. Synthesis,
Molecular Structure, and Spectroscopic Characterization of Dicarbollide Complexes
of Samarium and Ytterbium

by

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| <p>The interaction of $\text{Na}_2[\text{nido-7,8-C}_2\text{B}_9\text{H}_{11}]$ (1) with LnI_2 ($\text{Ln} = \text{Sm}, \text{Yb}$) in THF affords a complex with the composition $\text{Ln}(\text{C}_2\text{B}_9\text{H}_{11})(\text{THF})_4$ ($\text{Ln} = \text{Sm}$ (2), Yb (3)). Both these complexes have been fully characterized by spectroscopic techniques, and the molecular structure of the DMF derivative of 3 has been established by a single-crystal X-ray diffraction study. The DMF derivative, $\text{Yb}(\text{C}_2\text{B}_9\text{H}_{11})(\text{DMF})_4$ (3b), crystallizes in the orthorhombic space group $Pbca$ with $a = 10.208$ (1) Å, $b = 17.005$ (3) Å, $c = 31.627$ (5) Å, $V = 5479$ Å³, and $Z = 8$. Data were collected on a modified Picker FACS-1 diffractometer at 25 °C using Mo Kα radiation, to a maximum $2\theta = 50^\circ$, giving 4841 unique reflections, and the structure was solved by statistical methods. The final discrepancy index was $R = 0.082$, $R_w = 0.084$ for 1424 independent reflections with $I > 2\sigma(I)$. The dicarbollide ligand is η^3-bound to the Yb ion, and four DMF molecules are coordinated to Yb through the oxygen atoms. Complex 2 is fluxional in solution. The fluxionality of complex 2 in solution has been monitored by variable-temperature ¹¹B NMR spectroscopy, and a dynamic process involving the Sm^{2+} ion and the dicarbollide ligand has been proposed. The reaction of <i>closo</i>-1,1,1,1-(THF)₄-1,2,3-$\text{LnC}_2\text{B}_9\text{H}_{11}$ ($\text{Ln} = \text{Sm}$ (2), Yb (3)) with $[\text{PPN}]^+[\text{closo-3,1,2-TiC}_2\text{B}_9\text{H}_{11}]^-$ in THF produces $[\text{3,3-(THF)}_2\text{-} \text{closo-3,3'-Ln(3,1,2-LnC}_2\text{B}_9\text{H}_{11})_2]^-[\text{PPN}]^+$ ($\text{Ln} = \text{Sm}$ (4), Yb (5)), which has been characterized spectroscopically. The molecular structure of 4 has been established by an X-ray diffraction study. The complex 4 crystallizes in the triclinic space group $P\bar{1}$ with $a = 8.9374$ (3) Å, $b = 17.8703$ (6) Å, $c = 18.4989$ (7) Å, $\alpha = 107.5402$ (9)°, $\beta = 91.085$ (1)°, $\gamma = 90.705$ (1)°, $V = 2816$ Å³, and $Z = 2$. Data were collected at 25 °C on a diffractometer equipped with a small Huber circle, using Mo Kα radiation, to</p> | | | | | |
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Metallacarborane Complexes That Incorporate the Lanthanides. Synthesis, Molecular Structure, and Spectroscopic Characterization of Dicarborollide Complexes of Samarium and Ytterbium

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The interaction of $\text{Na}_2[\text{nido-7,8-C}_2\text{B}_9\text{H}_{11}]$ (1) with LnI_2 ($\text{Ln} = \text{Sm}, \text{Yb}$) in THF affords a complex with the composition $\text{Ln}(\text{C}_2\text{B}_9\text{H}_{11})(\text{THF})_4$ ($\text{Ln} = \text{Sm}$ (2), Yb (3)). Both these complexes have been fully characterized by spectroscopic techniques, and the molecular structure of the DMF derivative of 3 has been established by a single-crystal X-ray diffraction study. The DMF derivative, $\text{Yb}(\text{C}_2\text{B}_9\text{H}_{11})(\text{DMF})_4$ (3b), crystallizes in the orthorhombic space group $Pbca$ with $a = 10.208$ (1) Å, $b = 17.005$ (3) Å, $c = 31.627$ (5) Å, $V = 5479$ Å³, and $Z = 8$. Data were collected on a modified Picker FACS-1 diffractometer at 25 °C using Mo K α radiation, to a maximum $2\theta = 50^\circ$, giving 4841 unique reflections, and the structure was solved by statistical methods. The final discrepancy index was $R = 0.082$, $R_w = 0.084$ for 1424 independent reflections with $I > 2\sigma(I)$. The dicarborollide ligand is η^3 -bound to the Yb ion, and four DMF molecules are coordinated to Yb through the oxygen atoms. Complex 2 is fluxional in solution. The fluxionality of complex 2 in solution has been monitored by variable-temperature ¹¹B NMR spectroscopy, and a dynamic process involving the Sm^{2+} ion and the dicarborollide ligand has been proposed. The reaction of *closo*-1,1,1,1-(THF)₄-1,2,3- $\text{LnC}_2\text{B}_9\text{H}_{11}$ ($\text{Ln} = \text{Sm}$ (2), Yb (3)) with $[\text{PPN}]^+[\text{closo-3,1,2-TlC}_2\text{B}_9\text{H}_{11}]^-$ in THF produces $\{3,3-(\text{THF})_2\text{-}com\text{-}mo\text{-}3,3'\text{-Ln}(3,1,2\text{-LnC}_2\text{B}_9\text{H}_{11})_2\}^+[\text{PPN}]^-$ ($\text{Ln} = \text{Sm}$ (4), Yb (5)), which has been characterized spectroscopically. The molecular structure of 4 has been established by an X-ray diffraction study. The complex 4 crystallizes in the triclinic space group $P\bar{1}$ with $a = 8.9374$ (3) Å, $b = 17.8703$ (6) Å, $c = 18.4989$ (7) Å, $\alpha = 107.5402$ (9)°, $\beta = 91.085$ (1)°, $\gamma = 90.705$ (1)°, $V = 2816$ Å³, and $Z = 2$. Data were collected at 25 °C on a diffractometer equipped with a small Huber circle, using Mo K α radiation, to a maximum of $2\theta = 45^\circ$, giving 7358 unique reflections, and the structure was solved by a combination of conventional Patterson, Fourier, and full-matrix least-squares techniques. The final discrepancy index was $R = 0.053$, $R_w = 0.065$ for 5324 independent reflections with $I > 3\sigma(I)$. Both the dicarborollide ligands are η^3 -bound to the Sm ion in a nonparallel or bent fashion, and the coordination sphere about the Sm is completed by two THF molecules. The coordination geometry of 4 can be best described as a distorted tetrahedron. This is the first structurally authenticated example of a bis(dicarborollide)lanthanide complex. The structure of 4 is compared with related bis(cyclopentadienyl)lanthanides.

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